IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Diehl et al.
Serial No.: 10/612,288
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Examiner: Jennine M. Brown
Group Art Unit: 1755

For : HYDROTREATING CATALYST THAT CONTAINS A NITROGEN-CONTAINING ORGANIC COMPOUND AND ITS USE.

DECLARATION UNDER 37 C.F.R.§1.132

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir :

I, Slavik KASZTELAN, being duly warned, declare and say as follows:

THAT, I am a French citizen holding the titles of Engineer delivered by "Ecole des Hautes Etudes Industrielles de Lille" in 1982, of "Docteur ès Sciences" delivered by "Université de Lille" in 1984, residing at 69006 Lyon, France, 97 quai Charles de Gaulle.

THAT, I have been engaged on research by "Institut Français du Pétrole" in their Kinetics and Catalysis Department since 1988, where I have been continuously and actively in charge of researches in the fields of hydrocracking, hydroisomerization, dewaxing and hydrogenation of aromatic compounds. I was since September 2002 to April 2006 the manager of the Division "Catalysis and Separation". I am since May 1st, 2006, the Assistant Manager of the whole Refining and Petrochemical Division.

I declare further :

THAT, I am familiar with the contents of U.S. Patent Application Serial No 10/612,288.

THAT in order to support patentability of the present application, I have supervised the following experiments :

Example 15 : Preparation of a catalyst C10 such as NiMoP dried, with 2(2-amino ethyl amino)ethanol as an additive and comparison with the other methods of preparation in the hydrodesulphurization test of a gas oil and in hydrotreatment of vacuum distillate

The catalyst C10 is prepared in an identical way to that of catalyst C5, but the additive is added in the sulfidation feed comprising of direct distillation gas oil, 2% weight of dimethyldisulfure and 3000 ppm weight of 2(2-amino ethyl amino)ethanol. This sulfidation feed is replaced beyond 150°C, by a sulfidation feed comprising the same direct distillation gas oil and 2% weight of dimethyldisulfure and the sulfidation goes on before testing under gas oil and vacuum distillate.

Example 16 : Preparation of a catalyst C11 such as CoMoP dried, with 2(2-amino ethyl amino)ethanol as an additive and comparison with the other methods of preparation in the hydrodesulphurization test of a gas oil and in hydrotreatment of vacuum distillate

The catalyst C11 is prepared in an identical way to that of catalyst C1, but the additive is added in the sulfidation feed comprising of direct distillation gas oil, 2% weight of dimethyldisulfure and 3000 ppm weight of 2(2-amino ethyl amino)ethanol. This sulfidation feed is replaced beyond 150°C, by a sulfidation feed comprising the same direct distillation gas oil and 2% weight of dimethyldisulfure and the sulfidation goes on before testing under gas oil and vacuum distillate.

Example 17 : Preparation of a catalyst C12 such as NiMoP dried, with ethylenediamine as an additive wherein the additive is added in the sulfidation feed

The catalyst C12 is prepared in an identical way to that of catalyst C1, but the additive is added in the sulfidation feed comprising of direct distillation gas oil, 2% weight of dimethyldisulfure and 3,3 wt % of ethylenediamine. This sulfidation feed is replaced beyond 150°C, by a sulfidation feed comprising the same direct distillation gas oil and 2% weight of dimethyldisulfure and the sulfidation goes on before testing under gas oil and vacuum distillate.

Example 18 : Preparation of a catalyst C13 such as CoMoP dried, with ethylenediamine as an additive wherein the additive is added in the sulfidation feed

The catalyst C13 is prepared in an identical way to that of catalyst C1, but the additive is added in the sulfidation feed comprising of direct distillation gas oil, 2% weight of dimethyldisulfure and 3,7 wt % of ethylenediamine. This sulfidation feed is replaced beyond 150°C, by a sulfidation

feed comprising the same direct distillation gas oil and 2% weight of dimethyldisulfure and the sulfidation goes on before testing under gas oil and vacuum distillate.

Example 19 : Preparation of a catalyst C14 (according to example 1 of EP 0 164 162) such as NiMoP dried, with ethylenediamine as an additive

C14 was prepared with concentrations of 3,0 %wt NiO / 16,0 %wt MoO_3 / 7,3 wt% P_2O_5 supported on a gamma alumina carrier. A dry pore volume impregnation technique was used such that the support pores were just filled with a solution of the various salts. A solution suitable for impregnating 200 g of alumina with a pore volume of 0,75 cc/g was prepared as follows: Nickel nitrate hexahydrate (20,5 g) was dissolved in a 85% solution of phosphoric acid (28,6 g) and enough distilled water to provide approximately 50 ml of a first solution. To this solution was added 5,4 g of nickel carbonate (51,2%w Ni). The solution was stirred and heated gently (38°C) until all solids were dissolved, thereby providing approximately 60 ml of solution number 1. A second solution was made by mixing 11 ml of 30% hydrogen peroxide, 50 ml of distilled water and 44,1 g of ammonium heptamolybdate. The mixture was gently heated (38°C) until all solids were dissolved. To this was added 10,8 g of molybdenum trioxide and 1,2 g of ethylenediamine. The heating and stirring was continued until a clear yellow solution was obtained. When both solutions were at or near ambient temperature, solution number 2 was slowly added to solution number 1, while stirring. After cooling to approximately 32°C and diluting to 150 ml with water, the solution had a pH of about 2,2 (at 38°C). It was then added to a gamma alumina support in several small portions with intermediate agitation. The impregnated support was further agitated during 15-30 minutes, dried for 2 hours at 120°C and calcined in air for 2 hours at 480°C.
The catalyst is then sulfided by treatment with a H_2/H_2S (5%v H_2S) gaseous mixture at a temperature of 370°C for 2 hours.

Example 20 : Preparation of a catalyst C15 (according to example 1 of EP 0 164 162) such as CoMoP dried, with ethylenediamine as an additive

C15 was prepared with concentrations of 4,1 %wt CoO / 18,2 %wt MoO_3 / 5,0 wt% P_2O_5 supported on a gamma alumina carrier. A dry pore volume impregnation technique was used such that the support pores were just filled with a solution of the various salts. A solution suitable for impregnating 200 g of alumina with a pore volume of 0,75 cc/g was prepared as follows: Cobalt nitrate hexahydrate (28,2 g) was dissolved in a 85% solution of phosphoric acid (39,3 g) and enough distilled water to provide approximately 50 ml of a first solution. To this

solution was added 7,4 g of cobalt carbonate (51 %w Co). The solution was stirred and heated gently (38°C) until all solids were dissolved, thereby providing approximately 60 ml of solution number 1. A second solution was made by mixing 11 ml of 30 % hydrogen peroxide, 50 ml of distilled water and 50,2 g of ammonium heptamolybdate. The mixture was gently heated (38°C) until all solids were dissolved. To this was added 12,3 g of molybdenum trioxide and 1,4 g of ethylenediamine. The heating and stirring was continued until a clear yellow solution was obtained. When both solutions were at or near ambient temperature, solution number 2 was slowly added to solution number 1, while stirring. After cooling to approximately 32°C and diluting to 150 ml with water, the solution had a pH of about 2,1 (at 38°C). It was then added to a gamma alumina support in several small portions with intermediate agitation. The impregnated support was further agitated during 15-30 minutes, dried for 2 hours at 120°C and calcined in air for 2 hours at 480°C.

The catalyst is then sulfided by treatment with a H_2/H_2S (5%v H_2S) gaseous mixture at a temperature of 370°C for 2 hours.

Table 6 : Activity of catalysts in hydrodesulphurization of gas oil

The conditions of the test are identical as that of example 10.

Catalysts	A_{HDS} relative to C5
C5	100
C10	180
C11	175
C15	160

Table 7 : Activity of catalysts in hydrotreatment of vacuum distillate

The conditions of the test are identical as that of example 11

Catalysts	A_{HDS} relative to C5	A_{HDN} relative to C5	Conversion 380 °C $^-$ (%)
C5	100	100	25
C10	155	160	32
C12	150	155	31
C14	140	140	29

Surprisingly, table 6 and 7 show the significant gain of activity that is obtained on the catalysts prepared according to the invention relative to the catalyst according to the EP 0 164 162 process of preparation C14 and C15.

The undersigned declares further that all statements made herein of this own knowledge are true and that all statements made on information or belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 Title 18 of United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Solaize, January 11, 2006.

Slavik KASZTELAN